

(18)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) Publication number:

**0 104 807**

**B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 04.04.90

(51) Int. Cl.<sup>5</sup>: C 10 G 45/64

(71) Application number: 83305125.3

(72) Date of filing: 05.09.83

(54) Use of high pressure to improve product quality and increase cycle length in catalytic lube dewaxing.

(30) Priority: 28.09.82 US 425842

(43) Date of publication of application:  
04.04.84 Bulletin 84/14

(45) Publication of the grant of the patent:  
04.04.90 Bulletin 90/14

(84) Designated Contracting States:  
BE DE FR GB IT NL

(56) References cited:  
GB-A-2 010 321

(73) Proprietor: MOBIL OIL CORPORATION  
150 East 42nd Street  
New York New York 10017 (US)

(72) Inventor: Tabak, Samuel Allen  
204 East Pine Street  
Wenonah, NJ 08090 (US)  
Inventor: Shih, Stuart Shan-San  
7 Abinger Lane  
Cherry Hill, NJ 08003 (US)

(74) Representative: Cooper, John Anthony et al  
Mobil Court 3 Clements Inn  
London WC2A 2EB (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

**EP 0 104 807 B1**

## Description

This invention relates to the manufacture of high grade viscous oil products from crude petroleum fractions, particularly high quality lube base stock oils from crude stocks of high wax content, commonly classified as "wax base" as compared with the "naphthenic base" crudes. The latter crudes are relatively lean in straight chain paraffins and yield viscous fractions which inherently possess low pour points.

High quality lube base stock oils are conventionally prepared by refining distillate fractions or the residuum prepared by vacuum distilling a suitable crude oil from which the lighter portion has been removed by distillation in an atmospheric tower. Thus, the charge to the vacuum tower is commonly referred to as a "long residuum" and the residuum from the vacuum tower is distinguished from the starting material by referring to it as the "short residuum".

The vacuum distillate fractions are upgraded by a sequence of unit operations, the first of which is solvent extraction with a solvent selective for aromatic hydrocarbons. This step serves to remove aromatic hydrocarbons of low viscosity index and provides a raffinate of improved viscosity index and quality. Various processes have been used in this extraction stage, and these employ solvents such as furfural, phenol, sulfur dioxide and others. The short residuum, because it contains most of the asphaltenes of the crude oil, is conventionally treated to remove these asphalt-like constituents prior to solvent extraction to increase the viscosity index.

The raffinate from the solvent extraction steps contains paraffins which adversely affect the pour point. Thus, the waxy raffinate, regardless of whether prepared from a distillate fraction or from the short residuum, must be dewaxed. Various dewaxing procedures have been used and the art has gone in the direction of treatment with a solvent such as methyl ethyl ketone (MEK)/toluene mixtures to remove the wax and prepare a dewaxed raffinate. The dewaxed raffinate may then be finished by any of a number of sorption or catalytic processes to improve color and oxidation stability.

The quality of the lube base stock oil prepared by the sequence of operations outlined above depends on the particular crude chosen as well as the severity of treatment for each of the treatment steps. Additionally, the yield of high quality lube base stock oil also depends on these factors and, as a rule, the higher the quality sought, the less the yield. In general, naphthenic crudes are favored because less loss is encountered, particularly in the dewaxing step. In many cases, however, waxy crudes are more readily available and it would be desirable to provide a process for preparing high quality lube base stock oils in good yields from such waxy crude oils.

In recent years, processes for the selective hydrocracking of paraffinic components to lower molecular weight fragments employing a zeolite catalyst have been developed to accomplish the dewaxing of crude stocks of high wax content. Thus, for example, the lube oil dewaxing process of U.S. Patent No. 3,337,447 utilizes a cadmium-containing Zeolite A catalyst. In accordance with U.S. Patent No. 3,438,887, improved lubricating oils are prepared from waxy distillates by a sequence of solvent refining, catalytic dewaxing over the low sodium or acid form of mordenite containing a hydrogenating component such as a Group VIII metal and hydrofining. Similar catalytic dewaxing processes are described in U.S. Patent Nos. 3,539,498 and 3,684,684. The lube oil dewaxing process of U.S. Patent No. 3,620,963 employs a catalytic mixture of mordenite and a nickel-tin component.

Lately, the dewaxing of solvent refined waxy crude to provide high quality lube base stocks employing an aluminosilicate zeolite having a silica to alumina ratio greater than 12 and a constraint index of 1 to 12 as represented by the ZSM-5 class of zeolites has come into prominence. Illustrative of the foregoing is the combined catalytic dewaxing/catalytic hydrotreating process described in U.S. Patent No. 4,137,148. In accordance with this process, a fraction having an initial boiling point of at least 232°C (450°F) and a final boiling point less than 566°C (1050°F) is taken by distillation of a wax base crude. That fraction is solvent refined by counter current extraction with at least an equal volume of a selective solvent such as furfural. The furfural raffinate is subjected to catalytic dewaxing by mixing with hydrogen and contacting at 260°—357°C (500°—675°F) with a catalyst containing a hydrogenation metal and zeolite ZSM-5 or other aluminosilicate zeolite having a silica/alumina ratio above 12 and a constraint index of 1 to 12 and space velocity (LHSV) of 0.1 to 2.0 volumes of charge oil per volume of catalyst per hour. The effluent of catalytic dewaxing is then cascaded into a hydrotreater containing, as catalyst, a hydrogenation component on a non-acidic support, such as cobalt-molybdate or nickel-molybdate on alumina. The hydrotreater operates at 218° to 316°C (425° to 600°F), preferably 246° to 288°C (475° to 550°F), and space velocity like that of the catalytic dewaxing reactor. The reactions are carried out at hydrogen partial pressures of 1035—10350 kPa (150—1500 psia), at the reactor inlets, and preferably at 1725—3450 kPa (250—500 psia), with 89 to 890 l/l (500 to 5000 standard cubic feet) of hydrogen per barrel of feed (SCF/B), preferably 267 to 445 l/l (1500 to 2500 SCF/B). A configuration similar to that of U.S. 4,137,148, including cascading the dewaxer effluent to the hydrotreater, is described in G.B. 2,010,3212, and the hydrogen partial pressure exemplified therein (Example 1) is 400 psig for both the catalytic dewaxer and hydrotreater.

The hydrotreating step of the process of U.S. Patent No. 4,137,148 is essential if a lube base stock oil possessing adequate oxidation stability is to be obtained. In addition to the requirement of a hydrotreating step, it is necessary to reactivate the catalyst in this process before lined-out temperature operation is achieved since the lined-out temperature at the aforesaid operating pressures is well above 357°C (675°F), i.e., a temperature at which the oxidation stability of the final product begins to fall off significantly.

## EP 0 104 807 B1

It has now been discovered that by operating within a hydrogen partial pressure regime of at least 10350 kPa (1500 psia), dewaxing of a solvent refined wax base crude to provide a high quality lube base stock oil can be accomplished without the need for a separate hydrotreating step or hydrotreating catalyst as in U.S. Patent No. 4,137,148, *supra*.

In addition to eliminating the requirement for a separate hydrotreating step, the present process results in a significant lowering of the line-out temperature thereby extending catalyst life and reducing the frequency with which the dewaxing catalyst must be regenerated.

Accordingly, therefore this invention provides a process for preparing a high quality lube base stock oil having a pour point not higher than  $-1^{\circ}\text{C}$  ( $+30^{\circ}\text{F}$ ) from a waxy crude oil, which process comprises extracting distillate fraction that boils within the range of at least  $232^{\circ}\text{C}$  ( $450^{\circ}\text{F}$ ) to less than  $566^{\circ}\text{C}$  ( $1050^{\circ}\text{F}$ ) with a solvent selective for aromatic hydrocarbons to yield a raffinate; mixing the raffinate with hydrogen at pressure and contacting the mixture at a temperature of  $260^{\circ}$  to  $385^{\circ}\text{C}$  ( $500^{\circ}$  to  $725^{\circ}\text{F}$ ) with a dewaxing catalyst comprising a hydrogenation metal and an aluminosilicate zeolite having a silica/alumina ratio of at least about 12 and a constraint index of 1 to 12, thereby converting the wax contained in the raffinate to lower boiling hydrocarbons; and topping the dewaxed hydrotreated raffinate thereby recovering the high quality lube base stock oil, characterized in that the dewaxing is effected by contacting the raffinate with the dewaxing catalyst at a hydrogen partial pressure of at least 10,350 kPa (1500 psia) thereby improving cycle length of the catalyst.

The wax base crudes (sometimes called "paraffin base") from which the charge stock is derived by distillation constitute a well recognized class of crude petroleum. Many scales have been devised for classification of crude, some of which are described in Chapter VII Evaluation of Oil Stocks of "Petroleum Refinery Engineering," W. L. Nelson, McGraw-Hill, 1941. A convenient scale identified by Nelson at page 69 involves determination of the cloud point of the Bureau of Mines "Key Fraction No. 2" which boils between  $275^{\circ}\text{C}$  and  $300^{\circ}\text{C}$  ( $527^{\circ}\text{F}$  and  $572^{\circ}\text{F}$ ) at 40 mm pressure. If the cloud point of this fraction is above  $-15^{\circ}\text{C}$  ( $5^{\circ}\text{F}$ ), the crude is considered to be wax base.

According to the present invention, a propane deasphalted short residuum fraction or a fraction having an initial boiling point of at least  $232^{\circ}\text{C}$  ( $450^{\circ}\text{F}$ ) and a final boiling point less than  $566^{\circ}\text{C}$  ( $1050^{\circ}\text{F}$ ) is prepared by distillation of such wax base crude. That fraction is solvent refined by counter current extraction with at least an equal volume (100 vol.%) of a selective solvent such as furfural. It is preferred to use from 1.5 to 3.0 volumes of solvent per volume of oil. The furfural raffinate is subjected to catalytic dewaxing by mixing with hydrogen and contacting at  $260^{\circ}$ — $385^{\circ}\text{C}$  ( $500^{\circ}$ — $725^{\circ}\text{F}$ ) and a hydrogen partial pressure of above 10350 kPa (1,500 psia) and preferably at least 13800 kPa (2,000 psia) with a catalyst containing a hydrogenation metal and zeolite ZSM-5 or other aluminosilicate zeolite having a silica/alumina ratio above 12 and a constraint index of 1 to 12 and preferably a hydrogenation component, using a liquid hourly space velocity (LHSV) of 0.1 to 2.0 volumes of charge oil per volume of catalyst per hour. The preferred space velocity is 0.5 to 1.0 LHSV.

In some instances it may be desirable to partially dewax the charge stock, i.e., solvent-extracted raffinate, by conventional solvent dewaxing techniques, for example, to a pour point of from  $-12^{\circ}\text{C}$  ( $10^{\circ}\text{F}$ ) to  $10^{\circ}\text{C}$  ( $50^{\circ}\text{F}$ ). The higher melting point waxes so removed are those of higher market value than the waxes removed in conventionally taking the product to a still lower pour point below  $-12^{\circ}\text{C}$  ( $10^{\circ}\text{F}$ ).

The cracked (and hydrogenated) fragments from cracking wax molecules in the catalytic dewaxer will have adverse effects on flash and fire points of the dewaxed raffinate product and are therefore removed by distillation of the product to meet flash and fire point specifications.

The catalyst employed in the catalytic dewaxing reactor and the temperature in that reactor are important to success in obtaining good yields and very low pour point product. The hydrotreater catalyst may be any of the catalysts commercially available for that purpose but the temperature should be held within narrow limits for best results.

The solvent extraction technique is well understood in the art and needs no detailed review here. The severity of extraction is adjusted to the composition of the charge stock to meet specifications for the particular lube base stock and the contemplated end-use. This severity will be determined in practice of this invention in accordance with well established practices.

The dewaxing catalyst is a composite of hydrogenation metal, preferably a metal of Group VIII of the Periodic Table, associated with the acid form of a novel class of aluminosilicate zeolite having a silica/alumina ratio of at least about 12 and a constrained access to the intracrystalline free space, as more fully described hereinbelow.

An important characteristic of the crystal structure of this class of zeolites is that it provides constrained access to, and egress from the intracrystalline free space by virtue of having a pore dimension greater than 5 Angstroms and pore windows of about a size such as would be provided by 10-membered rings of oxygen atoms. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline aluminosilicate, the oxygen atoms themselves being bonded to the silicon or aluminum atoms at the centers of the tetrahedra. Briefly, the preferred type zeolites useful in this invention possess, in combination: a silica to alumina mole ratio of at least 12; and a structure providing constrained access to the crystalline free space.

The silica to alumina ratio referred to may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to

exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with a silica to alumina ratio of at least 12 are useful, it is preferred to use zeolites having higher ratios of at least 30. Such zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water, i.e., they exhibit "hydrophobic" properties. It is believed that this hydrophobic character is advantageous in the present invention.

The type zeolites useful in this invention freely sorb normal hexane and have a pore dimension greater than about 5 Angstroms. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of oxygen atoms, then access by molecules of larger cross-section than normal hexane is excluded and the zeolite is not of the desired type. Windows of 10-membered rings are preferred, although, in some instances, excessive puckering or pore blockage may render these zeolites ineffective. Twelve-membered rings do not generally appear to offer sufficient constraint to produce the advantageous conversions, although puckered structures exist such as TMA offretite which is a known effective zeolite. Also, structures can be conceived, due to pore blockage or other cause, that may be operative.

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access, a simple determination of the "constraint index" may be made by passing continuously a mixture of an equal weight of normal hexane and 3-methylpentane over a small sample, approximately 1 gram or less, of catalyst at atmospheric pressure according to the following procedure. A sample of the zeolite, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the zeolite is treated with a stream of air at 538°C (1000°F) for at least 15 minutes. The zeolite is then flushed with helium and the temperature adjusted between 288°C and 510°C (550°F and 950°F) to give an overall conversion between 10% and 60%. The mixture of hydrocarbons is passed at 1 liquid hourly space velocity (i.e., 1 volume of liquid hydrocarbon per volume of zeolite per hour) over the zeolite with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The "constraint index" is calculated as follows:

$$\text{Constraint Index} = \frac{\log_{10} (\text{fraction of n-hexane remaining})}{\log_{10} (\text{fraction of 3-methylpentane remaining})}$$

The constraint index approximates the ratio of the cracking rate constants for the two hydrocarbons. Zeolites suitable for the present invention are those having a constraint index in the approximate range of 1 to 12. Constraint Index (CI) values for some typical zeolites are:

CAS	C.I.
ZSM-5	8.3
ZSM-11	8.7
ZSM-12	2
ZSM-38	2
ZSM-35	4.5
TMA Offretite	3.7
Beta	0.6
ZSM-4	0.5
H-Zeolon	0.4
REY	0.4
Amorphous Silica-Alumina	0.6
Erionite	38

It is to be realized that the above constraint index values typically characterize the specified zeolites but that such are the cumulative result of several variables used in determination and calculation thereof. Thus, for a given zeolite depending on the temperature employed within the aforementioned range of 260° to 510°C (500° to 950°F), with accompanying conversion between 10% and 60%, the constraint index may vary within the indicated approximate range of 1 to 12. Likewise, other variables such as the crystal size of the zeolite, the presence of possible occluded contaminants and binders intimately combined with the zeolite may affect the constraint index. It will accordingly be understood by those skilled in the art that the constraint index, as utilized herein, while affording a highly useful means for characterizing the zeolites of interest is approximate, taking into consideration the manner of its determination, with probability, in some instances, of compounding variable extremes. However, in all instances, at a temperature within the above-specified range of 288° to 510°C (550°F to 950°F), the constraint index will have a value for any given zeolite of interest herein within the approximate range of 1 to 12.

The class of zeolites defined herein is exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-38, and other similar materials. U.S. Patent No. 3,702,886 describes ZSM-5, ZSM-11 is described in U.S. Patent No. 3,709,979, ZSM-12 is described in U.S. Patent No. 3,832,449, ZSM-35 is described in U.S. Patent No. 4,016,245, and ZSM-38 is described in U.S. Patent No. 4,046,859.

The specific zeolites described, when prepared in use presence of organic cations, are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 538°C (1000°F) for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 38°C (100°F) in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of this type zeolite; however, the presence of these cations does appear to favor the formation of this special type of zeolite. More generally, it is desirable to activate this type catalyst by base exchange with ammonium salts followed by calcination in air at about 538°C (1000°F) for from 15 minutes to 24 hours.

Natural zeolites may sometimes be converted to this type zeolite catalyst by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite, dachiardite, epistilbite, heulandite, and clinoptilolite. The preferred crystalline aluminosilicates are ZSM-5, ZSM-11, ZSM-12, ZSM-38 and ZSM-35, with ZSM-5 particularly preferred.

In a preferred aspect of this invention, the zeolites hereof are selected as those having a crystal framework density, in the dry hydrogen form, of not substantially below 1.6 grams per cubic centimeter. It has been found that zeolites which satisfy all three of these criteria are most desired. Therefore, the preferred zeolites of this invention are those having a constraint index as defined above of from 1 to 12, a silica to alumina ratio of at least about 12 and a dried crystal density of not less than about 1.6 grams per cubic centimeter. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g., on page 19 of the article on Zeolite Structure by W. M. Meier from "Proceedings of the Conference on Molecular Sieves, London, April 1967," published by the Society of Chemical Industry, London, 1968. When the crystal structure is unknown, the crystal framework density may be determined by classical pycnometer techniques. For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. It is possible that the unusual sustained activity and stability of this class of zeolites is associated with its high crystal anionic framework density of not less than about 1.6 grams per cubic centimeter. This high density, of course, must be associated with a relatively small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, is important as the locus of catalytic activity.

## EP 0 104 807 B1

Crystal framework densities of some typical zeolites are:

	Zeolite	Void volume	Framework density
5	Ferrierite	0.28 cc/cc	1.76 g/cc
10	Mordenite	.28	1.7
	ZSM-5, -11	.29	1.79
	Dachiardite	.32	1.72
15	L	.32	1.61
	Clinoptilolite	.34	1.71
20	Laumonite	.34	1.77
	ZSM-4 (Omega)	.38	1.65
	Heulandite	.39	1.69
25	P	.41	1.57
	Offretite	.41	1.55
30	Levynite	.41	1.54
	Erionite	.35	1.51
	Gmelinite	.44	1.46
35	Chabazite	.47	1.45
	A	.5	1.3
40	Y	.48	1.27

When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination of the ammonium form to yield the hydrogen form. In addition to the hydrogen form, other forms of the zeolite wherein the original alkali metal has been reduced to less than about 1.5 percent by weight may be used. Thus, the original alkali metal of the zeolite may be replaced by ion exchange with other suitable ions of Groups IB to VIII of the Periodic Table, including, for example, nickel, copper, zinc, palladium, calcium or rare earth metals.

In practicing the desired conversion process, it may be desirable to incorporate the above described crystalline aluminosilicate zeolite in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the zeolites employed herein may be composited with a porous matrix material such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix may vary widely with the zeolite content ranging from 1 to 99 percent by weight and more usually in the range of from 5 to 80 percent by weight of the composite.

# EP 0 104 807 B1

The effluent of the dewaxing unit is topped by distillation, i.e., the most volatile components are removed, to meet flash and fire point specifications.

While a hydrotreating step such as that described in U.S. Patent No. 4,137,148, *supra*, is ordinarily not required to provide a lube base stock oil having a suitable level of oxidation stability, in some cases it may be desirable to conduct such a step herein. In such case, the catalytic dewaxing effluent is introduced into a hydrotreater containing, as catalyst, a hydrogenation component on a non-acidic support, such as cobalt-molybdate or nickel-molybdate on alumina. Hydrotreating is effected therein at a temperature of from about 218° to 316°C (425° to 600°F), hydrogen partial pressures of 1035—10350 kPa (150—1500 psia), at the reactor inlets, and preferably 1725—3450 kPa (250—500 psia), with 89 to 890 l/l (500 to 5000 standard cubic feet) of hydrogen per barrel of feed (SCF/B), preferably 267 to 445 l/l (1500 to 2500 SCF/B).

The following examples illustrate the present invention. In the examples, all parts given are by weight unless specified otherwise.

## Examples 1—5

Examples 1 to 4 illustrate of the high-pressure catalytic dewaxing process of the present invention carried out upon two heavy neutral lube stocks, designated Raffinate A and Raffinate B, and Example 5 illustrates a low-pressure combined catalytic dewaxing/hydrotreating process such as described in U.S. Patent No. 4,137,148. In all examples, a nickel-containing HZSM-5 catalyst was employed.

Raffinates A and B possessed the properties set forth in Table I as follows:

TABLE I  
Feedstock properties

	Raffinate A	Raffinate B
Gravity, °API	29.7	29.4
Pour Point °C (°F)	46 (115)	49 (120)
Hydrogen, wt %	13.70	13.63
Sulfur, wt %	0.85	0.76
Nitrogen, wt %	0.03	0.03
Basic Nitrogen, ppm	47	30
CCR, wt %	0.06	0.05
KV, at 100°C, CS	9.4	11.1
Distillation, (Type D-1160) °C (°F)		
IBP	423 (793)	408 (766)
5%	454 (849)	471 (879)
10%	462 (864)	483 (902)
30%	480 (896)	501 (934)
50%	494 (921)	510 (950)
70%	508 (947)	521 (969)
90%	519 (966)	528 (982)
95%	545 (1013)	544 (1012)

The process conditions and yields for each example are set forth in Table II as follows:

# EP 0 104 807 B1

TABLE II  
Process conditions and yields  
(to -7°C (20°F) pour point 343°C (650°F+))

Operating conditions	1	2	Example 3	4	5
Raffinate	A	A	A	B	A
Pressure, kPa psia	13,800 2,000	13,800 2,000	13,800 2,000	13,800 2,000	2,760 400
Temperature, °C °F	304 579	362 684	369 697	371 699	303 577
LHSV	0.98	0.98	0.98	0.93	1.0
Catalyst Age, days on stream	4.7	17	23	30	—
H <sub>2</sub> Circulation, l/l scf/B	395.2 2,220	477.0 2,680	482.4 2,710	425.4 2,390	398.7 2,240
Process Yields					
H <sub>2</sub> S, Wt%	0.14	0.28	0.36	0.31	0.22
NH <sub>3</sub> , Wt%	0	0	0	0	0
C <sub>1</sub> —C <sub>3</sub> , Wt%	3.79	3.15	5.28	5.75	2.7
C <sub>4</sub> , Wt%	6.22	5.52	7.68	6.66	5.8
C <sub>5</sub> , Wt%	4.16	4.36	4.24	3.06	4.5
C <sub>6</sub> —166°C (330°F)	4.80	3.05	2.49	2.54	5.7
166°C—343°C (330—650°F)	3.32	4.79	4.65	5.07	
343°C+(650°F+)	77.89	79.37	75.02	76.96	81.5
Total	100.32	100.52	100.72	100.34	100.1
Hydrogen Consumption, l/l scf/b	33 185	53 300	74 415	35 197	20 115

## Claims

1. A process for preparing a high quality lube base stock oil having a pour point not higher than -1°C (+30°F) from a waxy crude oil, which process comprises extracting distillate fraction that boils within the range of at least 232°C (450°F) to less than 566°C (1050°F) with a solvent selective for aromatic hydrocarbons to yield a raffinate; mixing the raffinate with hydrogen at pressure and contacting the mixture at a temperature of 260° to 385°C (500° to 725°F) with a dewaxing catalyst comprising a hydrogenation metal and an aluminosilicate zeolite having a silica/alumina ratio of at least about 12 and a constraint index of 1 to 12, thereby converting the wax contained in the raffinate to lower boiling hydrocarbons; and topping the dewaxed hydrotreated raffinate thereby recovering the high quality lube base stock oil, characterized in that the dewaxing is effected by contacting the raffinate with the dewaxing catalyst at a hydrogen partial pressure of at least 10,350 kPa (1500 psia) thereby improving cycle length of the catalyst.
2. A process according to claim 1 wherein the topping is effected directly on the dewaxed raffinate thereby eliminating hydrotreating.
3. A process according to claim 1 or 2 wherein the hydrogen partial pressure is 13,800 kPa (2000 psia).
4. A process according to any preceding claim wherein the aluminosilicate zeolite comprises ZSM-5.
5. A process according to any preceding claim wherein the hydrogenation metal comprises nickel.
6. A process according to any preceding claim wherein the raffinate is partially dewaxed by solvent dewaxing before the catalytic dewaxing step.



## Patentansprüche

1. Verfahren zur Herstellung eines Schmierölgrundmaterials mit hoher Qualität und hohem Pourpoint von nicht größer als  $-1^{\circ}\text{C}$  ( $+30^{\circ}\text{F}$ ) aus einem paraffinischen Rohöl, wobei dieses Verfahren umfaßt:  
 5 Extraktion der Destillatfraktion, die im Bereich von mindestens  $232^{\circ}\text{C}$  ( $450^{\circ}\text{F}$ ) bis weniger als  $566^{\circ}\text{C}$  ( $1050^{\circ}\text{F}$ ) siedet, mit einem für aromatische Kohlenwasserstoffe selektiven Lösungsmittel, um ein Raffinat zu erzielen; Mischung des Raffinats mit Wasserstoff unter Druck und Kontakt dieser Mischung bei einer Temperatur von  $260$  bis  $385^{\circ}\text{C}$  ( $500$ — $725^{\circ}\text{F}$ ) mit einem Entparaffinierungskatalysator, der ein Hydrierungsmetall und einen Aluminosilikat-Zeolith mit einem Siliziumdioxid/Aluminiumoxid-Verhältnis  
 10 von mindestens etwa 12 und einem Zwangsindex von 1 bis 12 umfaßt, wodurch das im Raffinat enthaltene Paraffin in niedriger siedende Kohlenwasserstoffe umgewandelt wird; und Toppen des entparaffinierten hydrobehandelten Raffinats, wodurch das Schmierölgrundmaterial mit hoher Qualität gewonnen wird, dadurch gekennzeichnet, daß das Entparaffinieren durch Kontakt des Raffinats mit dem Entparaffinierungskatalysator bei einem Wasserstoffpartialdruck von mindestens  $10.350\text{ kPa}$  ( $1500\text{ psia}$ ) durchgeführt wird,  
 15 wodurch die Zykluslänge des Katalysators verbessert wird.
2. Verfahren nach Anspruch 1, worin das Toppen direkt am entparaffinierten Raffinat durchgeführt wird, wodurch die Hydrobehandlung eliminiert wird.
3. Verfahren nach Anspruch 1 oder 2, worin der Wasserstoffpartialdruck  $13.800\text{ kPa}$  ( $2000\text{ psia}$ ) beträgt.
4. Verfahren nach einem der vorstehenden Ansprüche worin der Aluminosilikat-Zeolith ZSM-5 umfaßt.
- 20 5. Verfahren nach einem der vorstehenden Ansprüche, worin das Hydrierungsmetall Nickel umfaßt.
6. Verfahren nach einem der vorstehenden Ansprüche, worin das Raffinat vor dem katalytischen Entparaffinierungsschritt durch Lösungsmittelentparaffinierung teilweise entparaffiniert wird.

## Revendications

1. Un procédé pour préparer une huile servant de charge de base pour des lubrifiants de haute qualité ayant un point de coulée ne dépassant pas  $-1^{\circ}\text{C}$  ( $+30^{\circ}\text{F}$ ) à partir d'un pétrole brut paraffinique, lequel procédé comprend l'extraction d'une fraction de distillat qui bout dans la gamme d'au moins  $232^{\circ}\text{C}$  à moins de  $566^{\circ}\text{C}$  ( $450$ — $1050^{\circ}\text{F}$ ) avec un solvant sélectif pour des hydrocarbures aromatiques afin de fournir un  
 30 raffinat; le mélange du raffinat avec de l'hydrogène, sous pression, et la mise en contact du mélange à une température de  $260^{\circ}\text{C}$  à  $385^{\circ}\text{C}$  ( $500$  à  $725^{\circ}\text{F}$ ) avec un catalyseur de déparaffinage comprenant un métal d'hydrogénation et une zéolite de type aluminosilicate ayant un rapport silice/alumine d'au moins environ 12 et un indice de contrainte de 1 à 12, de façon à convertir les paraffines contenues dans le raffinat en hydrocarbures de point d'ébullition inférieur; et l'enlèvement des têtes du raffinat hydrotraité déparaffiné  
 35 pour récupérer l'huile servant de charge de base pour des lubrifiants de haute qualité, caractérisé en ce que le déparaffinage est effectué par mise en contact du raffinat avec le catalyseur de déparaffinage à une pression partielle d'hydrogène d'au moins  $10.350\text{ kPa}$  ( $1500\text{ psia}$ ), si bien que la longueur du cycle du catalyseur est améliorée.
2. Un procédé suivant la revendication 1, caractérisé en ce que l'enlèvement des têtes est effectué  
 40 directement sur le raffinat déparaffiné, éliminant ainsi l'hydrotraitement.
3. Un procédé suivant la revendication 1 ou la revendication 2, caractérisé en ce que la pression partielle d'hydrogène est de  $13.800$  ( $2000\text{ psia}$ ).
4. Un procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que la zéolite de type aluminosilicate comprend la ZSM-5.
- 45 5. Un procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que le métal d'hydrogénation comprend du nickel.
6. Un procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que le raffinat est partiellement déparaffiné au cours d'un déparaffinage par solvant effectué avant l'étape de déparaffinage catalytique.

**THIS PAGE BLANK (USPTO)**